TWO NOVEL METHODS FOR ENHANCING SOURCE ZONE BIOREMEDIATION: DIRECT HYDROGEN ADDITION AND ELECTRON ACCEPTOR DIVERSION

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ABSTRACT: Two novel methods for enhancing bioremediation in DNAPL source zones are now being developed. The first method, direct hydrogen addition (i.e., electron donor addition without the use of fermentation substrates), is now being tested in the field by the Technology Transfer Division at the Air Force Center for Environmental Excellence (AFCEE). This approach permits the direct delivery of a relatively large mass of electron donor to DNAPL source zones undergoing biodegradation. The second method, electron acceptor diversion, is an emerging technology where competing electron acceptors are diverted around the source zone, thereby greatly increasing the naturally-occurring rate of reductive dechlorination in the source zone. This approach may have the potential to increase the naturally-occurring rate of DNAPL mass destruction at many sites without any long-term operating costs except monitoring.

INTRODUCTION

Hydrogen is now widely recognized as a key electron donor required for the biologically-mediated dechlorination of chlorinated compounds. Hydrogen acts as an *electron donor,* and halogenated compounds such as chlorinated solvents act as *electron acceptors* that are reduced in the reductive dechlorination process. To enhance beneficial anaerobic processes for the purpose of bioremediation, numerous research groups have focused on methods to increase the supply of electron donor to the dechlorinating bacteria. Most researchers and technology developers have focused on adding an indirect electron donor (such as lactate, molasses, mulch, edible oil, or other carbon source) that is fermented by one type of bacteria to produce hydrogen for the dechlorinators. However, there are two other methods to increase the effective supply of electron donor to the dechlorinating bacteria: 1) direct delivery of dissolved hydrogen to the subsurface (Hughes, et al. 1997); and 2) diversion of competing electron acceptors around the chlorinated solvent source zone (Newell et al., 2001).

DIRECT HYDROGEN DELIVERY

Direct delivery methods that have been proposed include circulation of groundwater containing dissolved hydrogen, placement of chemical agents that release dissolved hydrogen, electrolysis of water with subsurface electrodes, use

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of colloidal gas aphrons (foams), and low-volume pulsed biosparging (Hughes et al., 1997). Because of its simplicity and low-cost, AFCEE funded an 18-month long field trial of low-volume pulsed biosparging of hydrogen gas in the subsurface. With this approach, small volumes of hydrogen gas from cylinders was sparged directly into the contaminated zone in short intervals. In this case the sparge interval was approximately one 20 minute pulse once a week for most of the test. Small volumes are used to ensure that breakthrough to the surface will not present safety problems. The hydrogen is pulsed to allow effective dissolution of the trapped gas, thereby transferring the residual hydrogen gas to the aqueous phase.

Results from an eighteen-month low-volume pulsed hydrogen biosparging pilot test at Cape Canaveral Air Station Florida showed extensive biological dechlorination in a 30 x 30 ft (9.1 m x 9.1 m) zone located 15 to 20 ft (4.6 to 6 m) below the water table in a sandy aquifer. The test zone was in or very near a DNAPL source zone, as chlorinated ethene concentrations were very high (~300 mg/L). Hydrogen gas was pulsed into three sparge points at regular intervals (weekly for most of the test) to form residual hydrogen gas bubbles, which then dissolved to deliver electron donor directly to the test zone. Table 1 shows the observed changes in concentration in the test zone.

TABLE 1. Change in total chlorinated ethenes (CE) after 18 months of low-volume pulsed biosparging.

Location of Monitoring Well Group	Distance to Sparge Pts (ft)	Baseline CE Concentration (mg/L)	CE Concentration After 18 Months (mg/L)	Percent Change (%)
Close to Sparge Point	3 - 6	291	16	- 95%
Downgradient of Sparge	15	294	151	- 49%
Nitrogen Sparge Control	15	42	37	- 12%
Natural Attenuat. Control	20	207	165	- 20%

The change in the concentration in the test zone are presented in the following figures: TCE and cis 1,2-DCE (Figure 1); vinyl chloride and ethene (Figure 2); and methane (Figure 3). Figure 4 shows the vertical distribution of dissolved hydrogen in groundwater around the three hydrogen sparge points four days after a pulse event.

Wells in the hydrogen delivery zone showed greater reduction in chlorinated ethene concentrations compared to: 1) two wells (A-5 and B-5) located in a nitrogen control zone where nitrogen was pulsed into the subsurface at the same rate and frequency as the hydrogen sparge; and 2) two wells (A-1 and B-1) located in a natural attenuation control zone located outside the effective radius of the hydrogen sparge points. The greater reduction in chlorinated ethene concentrations in the hydrogen test monitoring wells compared to the control wells shows that reductive dechlorination resulted from the direct addition of hydrogen.

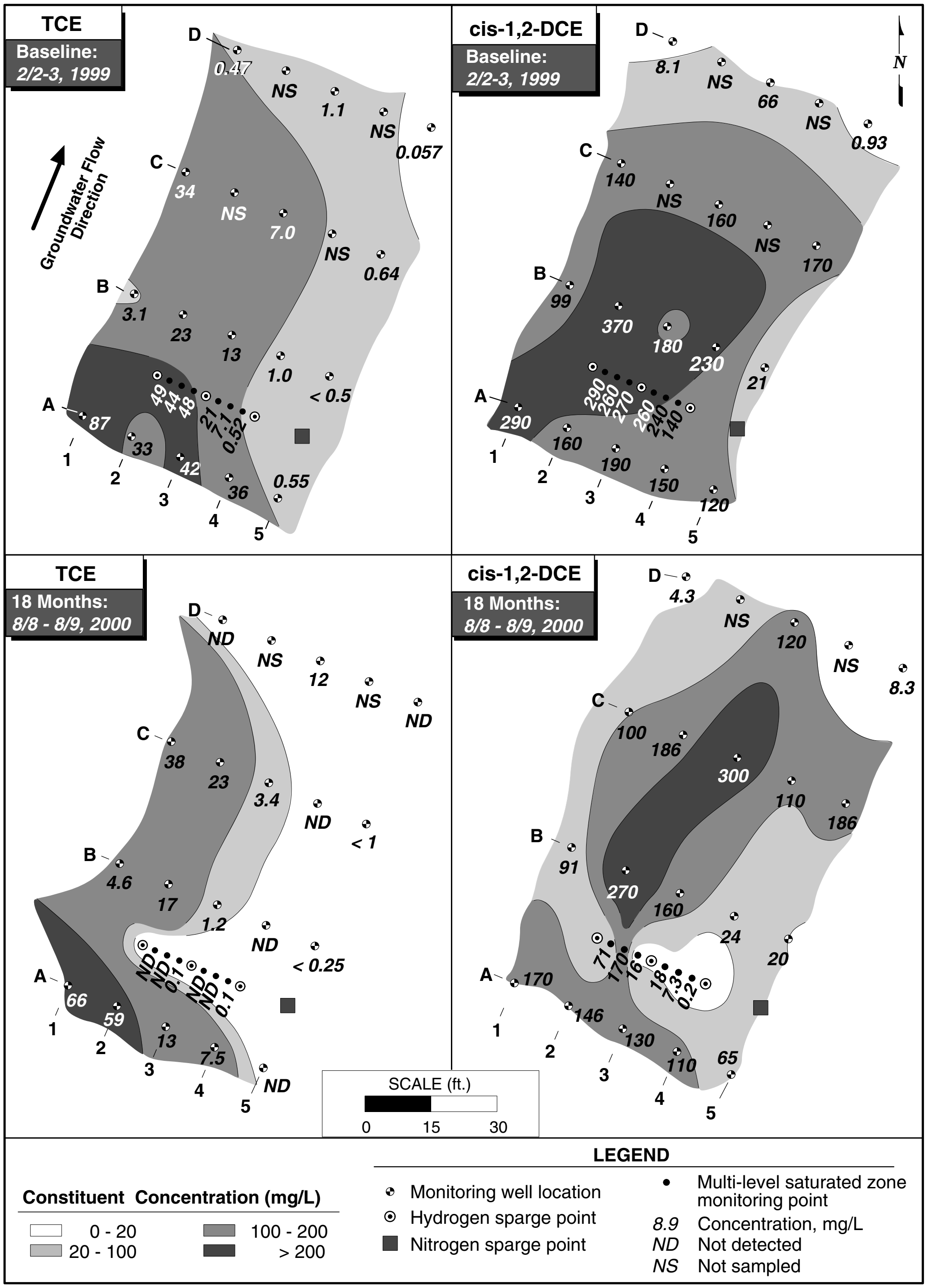

FIGURE 1. Change in TCE and cis-1,2-DCE concentration during 18-month pilot test of low-volume pulse biosparging Launch Complex 15, Cape Canaveral Air Station, Florida.

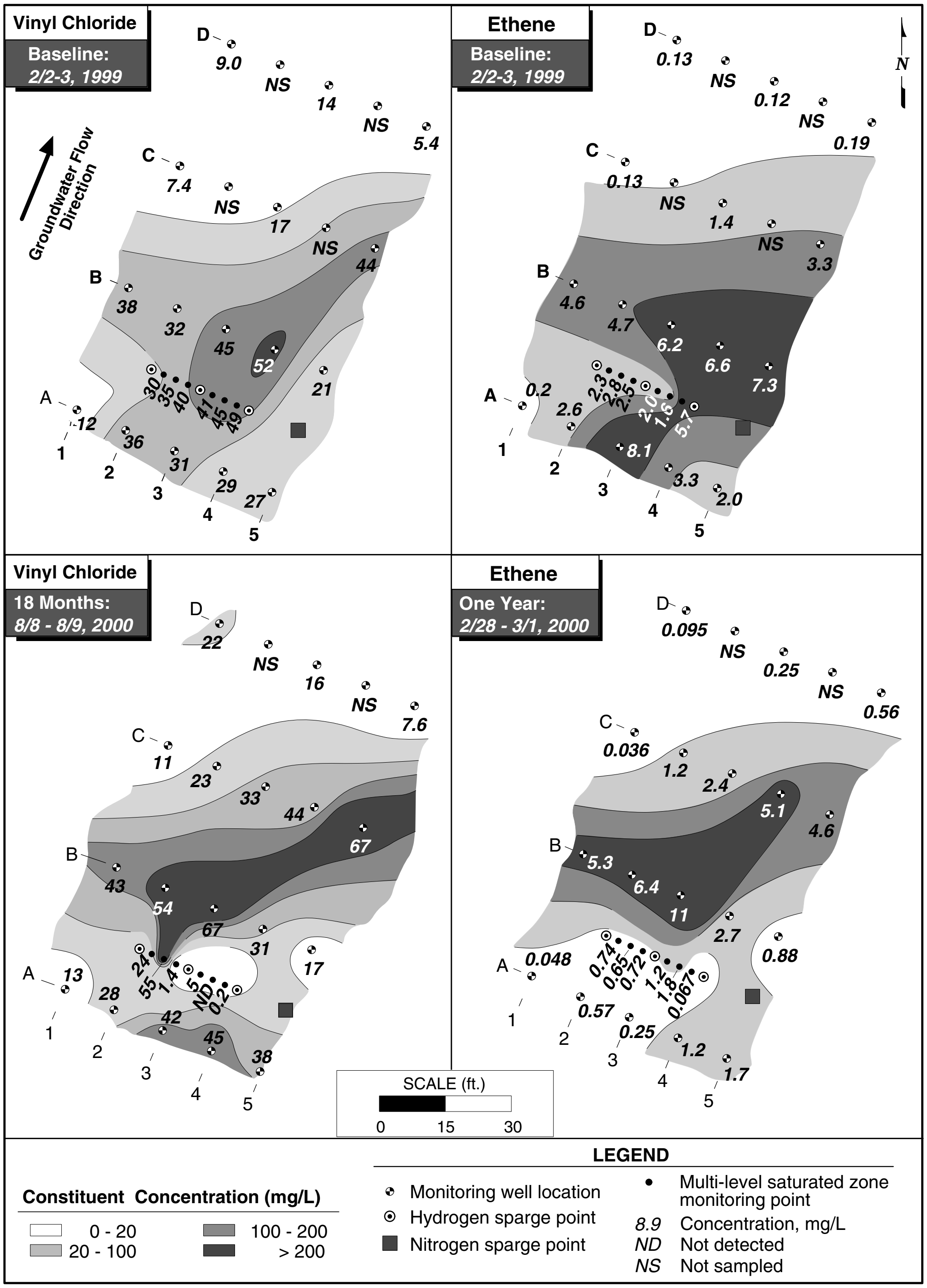

FIGURE 2. Change in vinyl chloride and ethene concentration during 18-month pilot test of low-volume pulse biosparging Launch Complex 15, Cape Canaveral Air Station, Florida

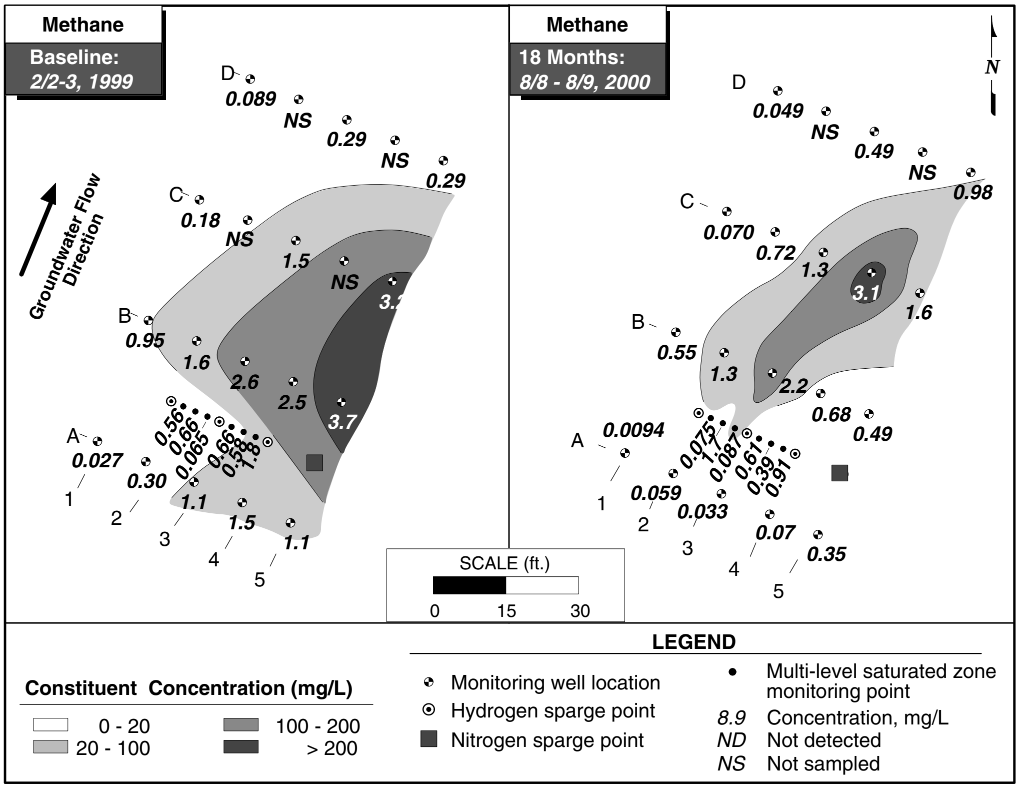

FIGURE 3. Change in methane concentration during 18-month pilot test of low-volume pulse biosparging

Evaluation of other indicators, such as the consumption of hydrogen vs. non-biodegraded tracers and increasing daughter/parent ratios, also support the conclusion that high rates of reductive dechlorination were initiated then sustained throughout the test zone by direct hydrogen delivery. No excessive methane production was observed during the test (see Figure 3), although increased concentrations of vinyl chloride were observed in the test zone after 18 months of treatment (see Figure 2).

DIVERSION OF COMPETING ELECTRON ACCEPTORS

The effective electron donor supply may be increased by reducing the transport of competing electron acceptors to a chlorinated solvent source zone (Newell et al., 2001). The presence of competing electron acceptors (primarily dissolved oxygen, nitrate, and sulfate) in a source zone will result in biodegradation reactions that compete with beneficial dechlorination reactions for

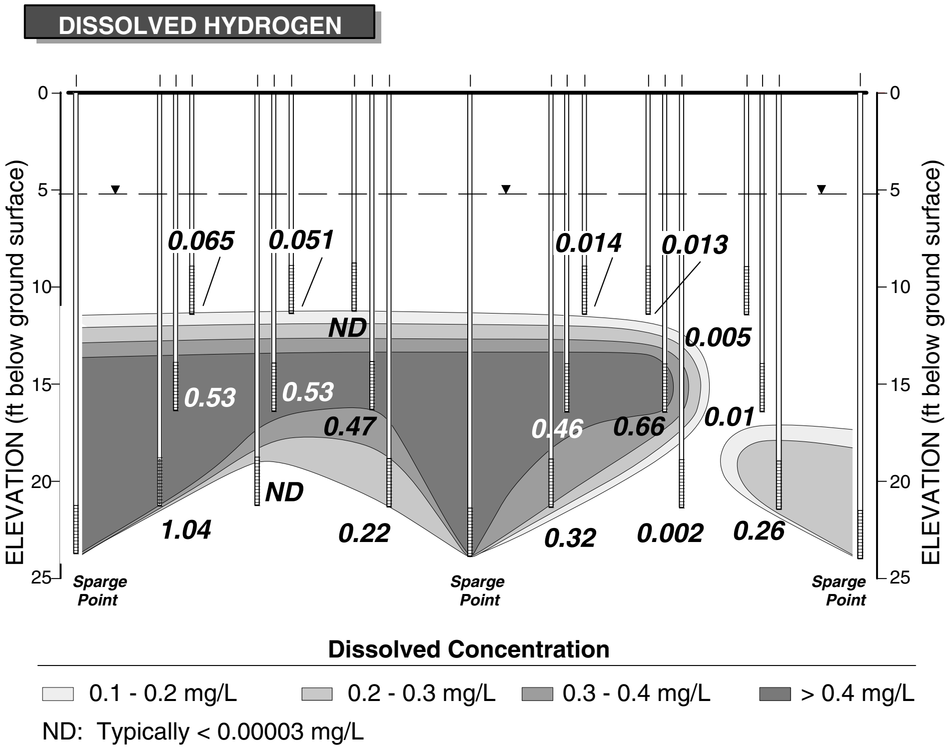

FIGURE 4. Vertical profile of dissolved hydrogen concentration in groundwater four days after weekly sparge event, 18 months after project startup. Gas mixture in last sparge event: 48% H_2, 48% He, 2% SF_6. Distance Between Sparge Points: 12 ft.

electron donor. This competition occurs in cases where the electron donor is present in the source zone prior to remediation (a Type I or Type II chlorinated solvent site; Wiedemeier et al., 1999) or if the electron donor supply is enhanced by adding fermentation substrates or hydrogen directly.

By diverting the transport of competing electron acceptors (oxygen, nitrate, and sulfate) around a contaminated groundwater zone in a Type I site (typically with anthropogenic donor in the source zone NAPL), the electron donor supply may be effectively increased. For example, a 14-site chlorinated site database in Wiedemeier et al. (1999) show the following characteristics (Table 2).

TABLE 2. Selected hydrogeologic, plume, and background groundwater characteristics from 14 chlorinated solvent sites.

	MEDIAN	STANDARD DEV.
Plume/source width	400 ft	604 ft
Seepage velocity	110 ft/yr	532 ft/yr
Saturated thickness	20 ft	19 ft
Background D.O.	8.0 mg/L	3.8 mg/L
Background NO3	5.8 mg/L	4.0 mg/L
Total Chlorin. Solvents in Source	1.5 mg/L	34 mg/L

Assuming a porosity of 0.3, a representative specific discharge through a chlorinated solvent source zone is equivalent to 15 x 10^6 L/yr of flow. Approximately 120 kg of dissolved oxygen and 87 kg of nitrate flow into a representative source zone per year, where they compete for electron donor. One method to account for the potential amount of lost reductive dechlorination to competing electron acceptors is to assume that every 16 kilograms of dissolved oxygen can consume the equivalent of 2 kilograms of dissolved hydrogen (based on the stoichiometry of water formation), and that every 50 kilograms of nitrate can consume the equivalent of 4 kilograms of dissolved hydrogen (based on the stoichiometry of nitrate reduction). Therefore the introduction of the 120 kilograms of dissolved oxygen and 87 kilograms of nitrate into the source zone per year is equivalent to the consumption of 22 kilograms of dissolved hydrogen per year (i.e., 120*2/16+87*4/50). Finally, if one uses the accepted stoichiometry where 1 kg of hydrogen has the potential to completely dechlorinate 21 kilograms of PCE, then an additional 462 kilograms of PCE could be completely dechlorinated to ethene per year assuming no loss to other mechanisms. Note this calculation does not account for sulfate as a competing electron acceptor, which would increase the potential benefits from electron acceptor diversion.

By comparison, naturally-occurring reductive dechlorination processes in a source zone at a typical chlorinated solvent site may be on the order of tens of kilograms per year. Using the BIOCHLOR natural attenuation model (Aziz et al., 2000a) with the representative site data above and a typical biodegradation rate coefficient for chlorinated solvents from the BIOCHLOR database (Aziz et al, 2000b), it is estimated that only 20 kilograms of solvents are biodegraded naturally per year in a 400 ft by 400 source zone.

Therefore diverting the competing electron acceptors away from the source zone has the potential to increase the biodegradation of chlorinated solvents in the source zone of a representative chlorinated solvent site from about 20 to 462 kilograms per year, greater than a 20-fold increase in the naturally-occurring biodegradation rate. Note that these calculations are estimates only and should be confirmed with detailed field measurements. This approach does have limitations, as it would not address vertical oxygen infiltration via diffusion or via rainfall, or remove competion from ferric iron in the source zone. The diversion of competing electron acceptors can be performed in a number of ways, but most likely can be achieved by the construction of a physical barrier upstream of the source zone using conventional geotechnical barrier techniques (slurry wall, grout curtain, etc.) (Figure 5).

In summary, by constructing a low-cost, low-permeability containment barrier upgradient of a chlorinated solvent source zone, three benefits may be realized: 1) competing electron acceptors will be diverted away from the source zone, thereby increasing the rate of naturally-occurring bioremediation; 2) the plume will shorten, greatly reducing long-term monitoring costs; and 3) the plume will be controlled without pumping. Such a barrier system will be inexpensive, reliable, and have the potential to significantly increase the rate of chlorinated solvent biodegradation at a typical chlorinated solvent site already undergoing natural attenuation.

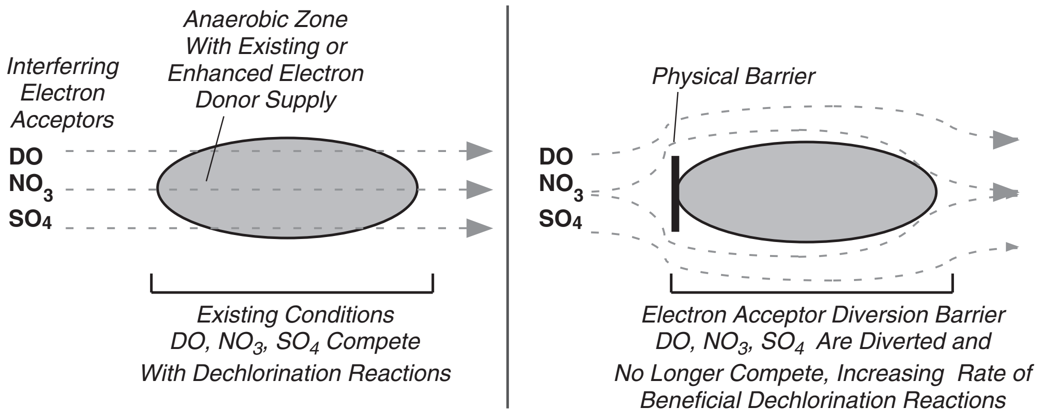

FIGURE 5. Conceptual diagram of physical barrier to divert competing electron acceptors.

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